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(54) **Control of grafting processes**

(57) A continuous-flow process in which side-chains are grafted to a thermoplastic base polymer, especially the grafting of side-chains suitable for hydrolytic crosslinking, is controlled with reference to a measured rheological property of the polymer. The melt property may be a true viscosity or a viscous modulus but any measurement that generates a number that correlates with viscosity can be used. The measurement is made on material at a place in the flow line where at least a substantial part of the grafting has taken place, preferably where it is (or ought to be) complete, and at least one reagent concentration or process condition is adjusted to maintain the measured property within limits that are preset, either absolutely or with reference to other prevailing conditions.

The grafting of polyethylene with vinyl trimethoxy silane in an extruder is described.

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~~CONTROL OF GRAFTING PROCESSES~~

This invention relates to the control of grafting processes and more particularly to the control of continuous-flow processes in which side-chains are grafted to a thermoplastic base polymer.

It relates especially (but not exclusively) to the control of the grafting of hydrolysable silane side-chains to carbon-chain polymers to permit a subsequent crosslinking of the polymers by reaction with water in the presence of a silane condensation catalyst (whether by the 2-stage "Sioplas E" process developed by Dow Corning Ltd (British Patent 1286460 and others) or by the single-stage adaptation developed by the present applications in conjunction with Établs. Maillefer SA (British Patent 1526398)). Grafting is generally initiated by a peroxide (or other free-radical generator) and the number of side-chains grafted to the polymer is very sensitive to the concentrations of initiator and of any contaminant that competes with or inhibits the grafting reaction (such as traces of acid in the silane), making quantitative control of the process difficult.

The invention also relates to the control of grafting by other techniques, including, for example, the grafting of silane side chains to an ester copolymer by a catalysed ester-exchange reaction.

It has long been known that grafting has a major influence on the rheological properties of a polymer melt, and we have now realised that this provides a valuable means of process control.

In accordance with the invention, a method for the control of a continuous-flow process in which side-chains are grafted to a thermoplastic base polymer comprises measuring at least one rheological property of the polymer either continuously or frequently at a place in the flow line where at least a substantial part of the grafting has taken place and adjusting at least one reagent concentration or process condition to maintain the measured property within pre-set limits.

The property or properties to be measured may be the true viscosity of the polymer (or of the composition containing it) under one or more standardised conditions of temperature and shear rate, or any convenient (and possibly arbitrary) number that sufficiently correlates with viscosity; for instance the melt flow index, the pressure drop across a flow passage under standardised conditions, the torque or force transmitted across a gap between relatively-moving bodies occupied by a suitably thin layer of the polymer, or the torque or force required to maintain motion under similar conditions. It may also be a more fundamental property, such as the viscous modulus of the material at some suitably chosen temperature, but the need for quick response may make

simpler properties preferable.

Preferably the measurement is made at a place in the process stream where the grafting reaction is (or ought to be) substantially complete. For example, in a grafting reation carried out in an extruder, measurement should be made in the latter part of the metering zone or in the extrusion head, or in a side stream bled off in a corresponding place. In some cases, it may be feasible to re-inject the stream after making the required measurements upon it, but in most cases it should be scrapped to avoid a risk of inhomogeneity in the product.

If a single rheological property only is measured, it will ordinarily only be possible to use it to regulate one reagent concentration or process variable, and the most useful one needs to be chosen for the particular process. For example, in the silane grafting process, we prefer to control the initiator (peroxide) concentration because of the known sensitivity of the process to this variable and the uncertainties of conventional control techniques. Other variables that might be controlled in this process include the silane concentration, extruder temperature and throughput rate.

However, by measuring two or more sufficiently different rheological properties it may be possible to control two or more variables, or at least to select on

the basis of the measurements and possibly automatically the variable that it would be most beneficial to adjust. For example, in the silane grafting reaction, both grafting itself (desirable) and premature crosslinking (undesirable) tend to raise the viscosity of the polymer composition under any one set of conditions, and a single measurement cannot distinguish the two effects. They can however be distinguished by measuring:

(i) viscosities under very different conditions of shear rate and/or temperature; or

(ii) viscosities at two different times (because crosslinking will continue during waiting time at relatively low temperature and grafting will not); or

(iii) viscous and elastic moduli

and the appropriate corrective action(s) taken (increased peroxide or temperature to overcome low rate of grafting, reduced moisture content to avoid premature crosslinking).

If the measurement conditions are sufficiently standardised, the pre-set limits may be fixed upper and lower limits of the directly measured property, but if measurements are made under varying conditions of temperature, pressure, shear rate or the like, limits will need to be tabulated or calculated according to the prevailing conditions.

Preferably measurements are fed directly to a process-control computer which effects the appropriate

adjustment(s), but in simpler cases at least it may be sufficient to display the measured value(s) for the plant operator to observe and make appropriate manual adjustments.

Example 1

This was a single-stage wire covering process using a polyethylene with a density 0.918 and MFI 2 and, per hundred parts of the polyethylene, 1.5 parts vinyl trimethoxy silane (VTMOS), nominally 0.1 part dicumyl peroxide, 0.5 parts of the stabiliser Flectol H (polymerised trimethyl dihydroquinoline) and 0.05 parts of the silanol condensation catalyst dibutyl tin dilaurate. These ingredients were fed to a Maillefer "30D" extruder having a diameter of 120 mm and an overall length:diameter ratio of about 30:1 and having a feed zone with a length of about 8 diameters in which the cross-section of the passage slowly decreases, followed by a homogenising zone of the kind subject of Maillefer's British Patent 964428 (now expired) occupying about six diameters in which, after an initial expansion, the material is forced over the flight of the screw from a rapidly-converging blind passage into a very slowly converging passage. This is followed by a slightly converging zone of about 6 diameters and finally a metering zone of uniform cross-section occupying the last 10 diameters of the length of the screw.

The barrel of the extruder was maintained at a temperature of 130°C up to and including the homogenising zone and part of the slightly converging section that follows it and at 230°C for the remainder of its length, including a wire-covering crosshead.

In applying the invention to this process, a small port was provided in the barrel of the extruder about one diameter from the outlet end of the metering zone and connected to a small gear pump which withdrew polymer at a uniform rate of 1000 $mm^3/s$ and fed it to a dynamic rheometer of the kind sold by Rheometrics Inc under the designation "ROR", which was thermostatted to 190°C and operated at a fixed shear rate of 1 $s^{-1}$. The dynamic viscosity was displayed, and the rate of supply of peroxide adjusted (when possible) to keep it always in the range 1.5 to 2.4 x $10^4$ poise (corresponding approximately to MFI 0.5 to 0.3) to give a very uniform product (with a gel content of about 77% after curing for 16 hours in water at 90°C) despite variations in the acidity of the VTMOS. When adjustment proved incapable of holding the viscosity in the pre-set range, it normally indicated that the feed mechanism for the peroxide (or some other ingredient) was not functioning correctly, and the process was shut down until corrective action was taken.

Example 2

This was similar to Example 1 except that the material flowing from the rheometer to waste was passed through a 15 mm internal diameter duct 1 m long, giving a dwell time of about 10 minutes, and then through a second identical viscometer operating in the same way (all thermostatted at 190°C). The two rheometers should give approximately the same reading, and any substantial increase in the reading of the second relative to the first indicates that premature cross-linking is taking place and the drying of ingredients needs attention.

Example 3

This was similar to Example 1, except that the rheometer was operated in a scanning mode to determine a viscosity/shear rate characteristic for a succession of samples taken at 10 minutes intervals, and the output taken to a process-control computer and utilised (with other measurements) to control not only the rate of addition of peroxide but also the speed of the extruder screw and the temperature of the metering zone.

Example 4

The machinery was similar of Example 1 except that a cross-head cavity transfer mixer was used to pigment the wire covering. A torque meter was fitted to the separate drive of the cavity transfer mixer and had previously been calibrated under standard conditions of temperature, rotational speed and flow rate, using

specimens of various polyethylenes without any compounding ingredients, to give a reading directly representing the melt flow index. Peroxide input was adjusted to keep this MFI reading in the range 0.3 to 0.5.

Example 5

Graft polymer for a two-stage silane crosslinking process was made using a standard PVC extruder fitted with a granulator head and a small sample was bled off at the outlet end of the extruder barrel and fed by a gear pump through an elongate slit passage. Two pressure transducers were inserted at spaced positions along the passage, and under pre-set conditions of temperature and flow rate the difference between the outputs of the two transducers represents the pressure drop across the part of the passageway between them and thus gives an arbitrary number related to the melt viscosity; the allowable range of variation in this number is determined by trial for each formulation, or by comparison with the numbers observed using polyethylenes of known MFI (without grafting ingredients): for example, if the polyethylene used has an initial nominal MFI of 8 and is compounded with 2.0 parts of VTMOS, nominally 0.25 part dicumyl peroxide and 0.5 parts of Flectol H (per hundred parts of polymer), polyethylenes of MFI 0.5 and 2 will indicate suitable limiting values.

Claims

1. A method for the control of a continuous-flow process in which side chains are grafted to a thermoplastic base polymer comprising measuring at least one rheological property of the polymer either continuously or frequently at a place in the flow line where at least a substantial part of the grafting has taken place and adjusting at least one reagent concentration or process condition to maintain the measured property within pre-set limits.

2. A method as claimed in Claim 1 in which the property measured is selected from:

(a) the viscosity of the polymer under one or more standardised conditions of temperature and shear rate

(b) Melt flow index;

(c) the pressure drop across a flow passage under standardised conditions

(d) the torque or force transmitted across a gap between relatively moving bodies occupied by a thin layer of the polymer

(e) the torque or force required to maintain motion between bodies defining between them a gap which is occupied by a thin layer of the polymer, or

(f) the viscous modulus of the material at a chosen temperature.

3. A method as claimed in Claim 1 or Claim 2 comprising measuring at least two different rheological

properties and utilising both measurements to determine the adjustment to be made.

4. A method as claimed in Claim 3 in which the two variables are

(a) viscosities under different conditions of shear rate and/or temperature,

(b) viscosities at two different times, or

(c) viscous and elastic moduli.

5. A method for the control of a continuous-flow process in which side-chains are grafted to a thermoplastic base polymer substantially as described with reference to any one of the numbered examples.

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